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CONTAMINANT REMOVAL FROM SEWAGE PLANT EFFLUENTS BY FOAMING

Jacques J. Weinstock

Radiation Application, Incorporated
Long Island City, New York

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Prepared for
U.S. Department of Health, Education and Welfare
Public Health Service
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Contract No. SAph 76555
Final Contract Report
for Period from June 1963-May 1964

October 1964

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LEGAL NOTICE

This report, the _____in a series being published to present significant findings in water renovation achieved under the Advanced Waste Treatment Research Program, was submitted in fulfilment of a contract (Contract No. SAph 76555) between Radiation Applications Incorporated and the Public Health Service. While overall guidance of the project was provided by the Advanced Waste Treatment Research Program, the results obtained, opinions expressed, and conclusions reached, are those of the author and are not necessarily endorsed by the Department of Health, Education, and Welfare. Except for editorial review, this report appears as presented.

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1. ABSTRACT

In the third and final year of a research and development program evaluating the use of foaming techniques to remove contaminants from sewage plant effluents, the following advances were realized:

a. A number of additives were evaluated for improving the effectiveness of foaming in lowering the ABS and COD levels in effluents. UCAR C-149 and Primafloc C-7 cationic polyelectrolytes were shown to be particularly effective in improving COD reductions.

b. The process variables relating to the use of additives were studied and optimized for the effluents (both primary and secondary) of two sewage treatment plants.

c. The effluents of five additional, widely separated sewage plants were studied, and the resulting data were used in unsuccessful efforts to develop satisfactory correlations describing the effects of air and effluent flow rates on ABS and COD removals by foaming.

d. Attempts to obtain samples of industrial wastes for foaming studies were largely unsuccessful, and the two samples which were obtained did not respond particularly well to foaming (black liquor and de-inking washer water from the pulp and paper industry).

2. INTRODUCTION

This report covers the third and final year of research and development under Contract No. SAph 76555 on the use of foaming techniques to remove refractory contaminants from sewage plant effluents.

The first year of this program demonstrated the feasibility of using foaming to reduce the ABS and COD concentrations in secondary effluents from sewage treatment plants.[1] General limits for these reductions were determined for both batch and continuous foaming, the latter technique resulting in ABS concentrations as low as 0.3 ppm and COD diminutions up to 40%. It was also shown that foaming had little or no effect on the concentrations of chloride ion and total solids, and that the volume reduction attained was very dependent on foaming apparatus design and on other operating variables.

The second year's work[2] examined in considerably more detail the effects of process variables. The effects of liquid residence time, air-to-liquid feed rate ratios, and bubble size on ABS removal were studied using a synthetic effluent. Using actual primary and secondary effluents the effects of residence time, foam height, and foam tube diameter on ABS and COD removals and on volume reduction were described. It was also demonstrated during the second year that certain additives (cationic polyelectrolytes) enhanced COD removal during foaming.

During the final year of the program, a number of cationic polyelectrolytes were studied with primary and secondary effluents at several concentrations. The effect of air-to-liquid ratio has also been examined on effluents from a total of seven sewage treatment plants, as well as the

effectiveness of the best additive found on improving ABS and COD removals from these effluents.

3. SCREENING OF ADDITIVES

It has been demonstrated previously[2] that a cationic type polyelectrolyte additive considerably enhances the contaminant removal capabilities of the foaming process. Specifically, foaming primary effluents containing 5 ppm UCAR Resin C-149 with air-to-effluent flow rate ratios of 5 to 7 and a residence time of 5 minutes, resulted in 45 to 70 percent COD removal and an additional improvement in ABS removal. The potential advantages and applicability of the foaming process were thus increased considerably. In fact, these initial data indicate that foaming with additives could act as a process intermediate between primary and secondary treatment, giving removals approaching those of secondary treatment in some cases. This could be attractive since a residence time of only 5 minutes or less is required for the foaming process compared with six hours for the activated sludge process.

The cationic polyelectrolytes, such as UCAR Resin C-149, are water soluble polymers having a polycationic character. These materials provide electropositive sites which can bridge or bind fine particles together into stable flocs. For this particular application the cationic polyelectrolytes must be capable of flocculating the negatively charged organic suspended and colloidal solids present in sewage effluents into floatable flocs. It is believed therefore that froth flotation plays a more important part in the improved COD removal from the modified sewage effluents by foaming than does foam separation.

The experimental work described in this Section represents an evaluation of the most effective commercial additives capable of enhancing contaminant removal from sewage effluents by foaming. The various additives were obtained as

samples from various manufacturers. Most of these additives are available in production or semi-production quantities, and a few only in research quantities.

3.1 Experimental Results

Table 1 lists the particular additives used. Five milligrams of additive per liter of effluent were used in these screening experiments. This concentration was somewhat arbitrarily chosen on the basis of previous successful experiments with UCAR Resin C-149, and, in addition, it lies within the concentration range recommended by most manufacturers. The effect of additive concentration is discussed in Section 4.1.1 below.

The experimental results, presented in Table 2, show that of the additives tested, only 3 give significant improvements in COD removal during foaming: UCAR C-149, its surface active analog SAC-154, and Primafloc C-7. These three give COD reductions of about 50% or more at the experimental conditions used compared with an average reduction of 15-20% for the experiments using no additives. All of the other additives studied appear to be relatively ineffective at this concentration.

Table 1

Additives Used in Experimental Foaming of Sewage Effluents

Commercial Name	Manufacturer	Active Ingredient
UCAR Resin C-149	Union Carbide	Cationic Polyelectrolyte
SAC-154	Union Carbide	Surface-active analog of UCAR Resin C-149
Flocculant 674	Dow Chemical	Cationic Polyelectrolyte
Primafloc C-3	Rohm & Haas	Cationic Polyelectrolyte
Primafloc C-5	Rohm & Haas	Cationic Polyelectrolyte
Primafloc C-6	Rohm & Haas	Cationic Polyelectrolyte
O'B Floc	O'Brien Industries	Nonionic Polyelectrolyte
Gantrez AN-169	General Aniline	Methyl Vinyl Ether/ Maleic Anhydride Copolymers
Nalco 600	Nalco Chemical	Cationic Polyelectrolyte
Nalcolite 605	Nalco Chemical	Cationic Polyelectrolyte
Nalcolite 670	Nalco Chemical	Water Soluble Polymer
BTC 776	Onyx Chemical	Dimethyl Benzyl Ammonium Chloride
Polyox WSR-301	Union Carbide	Water Soluble Ethylene Oxide Polymer
Polyox WSR-35	Union Carbide	Water Soluble Ethylene Oxide Polymer
Flocculant 614	Dow Chemical	Cationic Polyelectrolyte
Primafloc C-7	Rohm & Haas	Cationic Polyelectrolyte

Table 2

Screening of Additives for Use in Foaming Sewage Effluents

Conditions common to all experiments:
Feed: Primary Effluents from Bowery Bay Sewage Treatment Plant
Air Flow Rate = 390 ml/min.
Feed Flow Rate = 56 ml/min.
G/F = 7.0
Residence Time = 8.3 min.
Additive Concentration = 5 ppm (with exceptions noted)

Date	Sample	Additive Used	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR dimensionless
5-20-63	Feed	-	1.8	310	1115	2336	-	-
	Bottoms	None	0.7	248				690
	"	Primafloc C-5	0.7	256				318
	"	Primafloc C-3	0.6	243				485
	"	UCAR C-149	0.3	144				-
5-27-63	Feed	-	1.6	342	862	-	106	-
	Bottoms	None	0.7	284				815
	"	Primafloc C-5	0.7	271				635
	"	Primafloc C-3	0.5	266				670
	"	SAC-154	0.4	179				1400
5-31-63	Feed	-	1.3	343	1024	2350	170	-
	Bottoms	None	0.4	298				730
	"	Flocculant 674	0.5	276				505
	"	OB Floc	0.5	313				1290
6-4-63	Feed	-	1.1	252	689	1650	144	-
	Bottoms	None	0.4	199				470
	"	Flocculant 674	0.3	183				470
	"	OB Floc	0.4	218				430

continued

Table 2 (Continued)

Date	Sample	Additive Used	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR dimensionless
6-6-63	Feed	-	1.1	333	627	1589	200	-
	Bottoms	None	0.7	261				355
	"	Gantrez AN-169	0.5	252				480
	"	Gantrez AN-4651	0.5	253				365
6-11-63	Feed	-	1.0	321	751	1648	118	-
	Bottoms	None	0.5	261			119	430
	"	Gantrez AN-169	0.5	271			130	610
	"	Gantrez AN-4651	0.3	261			144	470
6-13-63	Feed	-	1.3	361	1110	2231	146	-
	Bottoms	None	0.5	291			130	515
	"	Nalco 600	0.6	287			92	435
	"	Nalcolyte 605	0.5	279			96	355
6-18-63	Feed	-	1.3	309	1196	-	70	-
	Bottoms	None	0.4	251			92	320
	"	Nalco 600	0.4	258			84	280
	"	Nalcolyte 605	0.6	255			52	335
6-21-63	Feed	-	1.3	282	882	1970	63	-
	Bottoms	None	0.5	215			67	1800
	"	BTC 776	0.3	235			57	-
	"	Nalcolyte 670	0.4	241			51	1850
6-26-63	Feed	-	1.1	291	927	2066	89	-
	Bottoms	None	0.5	252			91	590
	"	BTC 776	0.4	267			81	-
	"	Nalcolyte 670	0.6	247			101	1570

continued

Table 2 (Continued)

Date	Sample	Additive Used	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR dimensionless
6-28-63	Feed	-	1.2	318	867	1994	141	-
	Bottoms	None	0.6	312			132	-
	"	Polyox WSR-35	0.6	309			123	595
	"	Polyox WSR-301	0.4	389			103	1230
7-3-63	Feed	-	1.4	218	1050	2276	84	-
	Bottoms	None	0.7	195			85	1120
	"	Polyox WSR-35	0.5	181			87	280
	"	Polyox WSR-301	0.5	209			77	250
7-22-63	Feed	-	1.0	234	844			-
	Bottoms	None	0.6	197				1430
	"	Primafloc C-7	0.25	136				810
	"	Primafloc C-6	0.7	212				783
9-25-63	Feed[a]	-	2+	147	776	1751	197	-
	Bottoms	None	0.6	99			148	122
	"	Flocculant 614[b]	0.5	98			107	106
	"	SAC-154[b]	0.5	72			70	105

Notes: a
Secondary effluent sample from Bowery Bay Plant used for these runs.
b
Additive concentration = 10 ppm.

4. STUDY OF PROCESS VARIABLES IN THE FOAMING OF SEWAGE PLANT EFFLUENTS

4.1 Effects Related to Additives

4.1.1 Additive Concentration

Table 3 contains data showing the effect of polyelectrolyte concentration on its efficiency in promoting COD removal.

Experiments conducted on 7-9 and 7-15 show clearly that UCAR Resin C-149 gives a minimal improvement in COD removal at a concentration of 1 mg/liter, that this effect is somewhat improved at 3 mg/liter, and that a marked reduction in COD occurs when 10 mg/liter are used. The percentage COD reductions experienced in these two sets of experiments (averaged) are 21% with no additive, 31% with 1 ppm, 43% with 3 ppm, and 76% with 10 ppm. An intermediate concentration, 5 ppm, used in the additive screening studies described above gave 54% COD reduction. These data are graphically shown in Figure 1, indicating that the improvement in COD removal to be gained from UCAR C-149 increases almost linearly through 5 ppm and drops off only slightly from linearity at 10 ppm. Experiments conducted on 7-29 used Primafloc C-7 as the additive and showed COD reductions of 75% and 81% at C-7 concentrations of 10 and 15 ppm, respectively, compared with a 15% reduction with no additive. This same coagulant gave a 42% COD reduction at a concentration of 5 ppm during the screening experiments listed in Table 2-(on a different sample of primary effluent).

Thus, considering experimental error and variations in effluent samples from day to day, these two additives seem to produce roughly equal improvements in COD reduction at equal concentrations.

The experiments performed on 8-5 and 8-9 examined the

Table 3

Effect of Additive Concentration

Bowery Bay Sewage Treatment Plant, Primary Effluents
Air rate, G, = 390 ml/min.
Feed rate, F, = 56 ml/min
G/F = 7.0
Residence time, t_r, 8.3 min.

Date	Sample[a]	Additive Used: Name	Additive Used: Conc. ppm	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR dimensionless	Notes
7-9-63	F	-	-	1.2	300	674			-	-
	B_1	None	-	0.4	224				49	d
	B_2	UCAR C-149	1	0.4	200				28	-
	B_3	UCAR C-149	3	0.2	167				28	-
	B_4	UCAR C-149	10	0.2	65				6	b
7-15-63	F	-	-	0.9	193	1148			-	-
	B_1	None	-	0.3	161				74	d
	B_2	UCAR C-149	1	0.3	137				32	d
	B_3	UCAR C-149	3	0.25	113				69	-
	B_4	UCAR C-149	10	0.15	52				28	b
7-29-63	F	-	-	2.0	267	998	2048	214	-	-
	B_1	None	-	1.0	228			194	350	-
	B_2	Primafloc C-7	10	0.2	67			0	544	b
	B_3	Primafloc C-7	15	0.15	52			0	892	b
8-5-63	F	--	-	1.4	225	615	1490	162	-	-
	B_1	None	-	0.7	181			164	504	-
	B_2	Flocculant 614	10	0.4	160			150	361	c
	B_3	Flocculant 614	15	0.4	132			112	292	c

continued

Table 3 (Continued)

Date	Sample[a]	Additive Used: Name	Additive Used: Conc. ppm	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR dimensionless	Notes
8-9-63	F	-	-	1.9	e	980	2388	218	-	-
	B_1	None	-	0.6	e			180	397	-
	B_2	Nalcolyte 605	10	0.2	470			213	254	-
	B_3	Nalcolyte 605	15	0.2	233			120	427	c
	B_4	Primafloc C-5	15	0.2	193			124	560	b
8-28-63	F	-	-	1.5	382	1241	2855	255	-	-
	B_1	None	-	0.8	343	1227	2772	232	292	-
	B_2	UCAR C-149	5	0.4	358			15	1400	b,c B_1 used as Feed
	B_3	UCAR C-149	5	0.3	275			76	398	b,c regular feed

a
F = feed, effluent used
B_1 = composite bottoms sample taken after 6 and 8 residence times during first run with the particular feed effluent
B_2, B_3, etc. = same as B_1 except for second, third, etc., runs with the same feed.

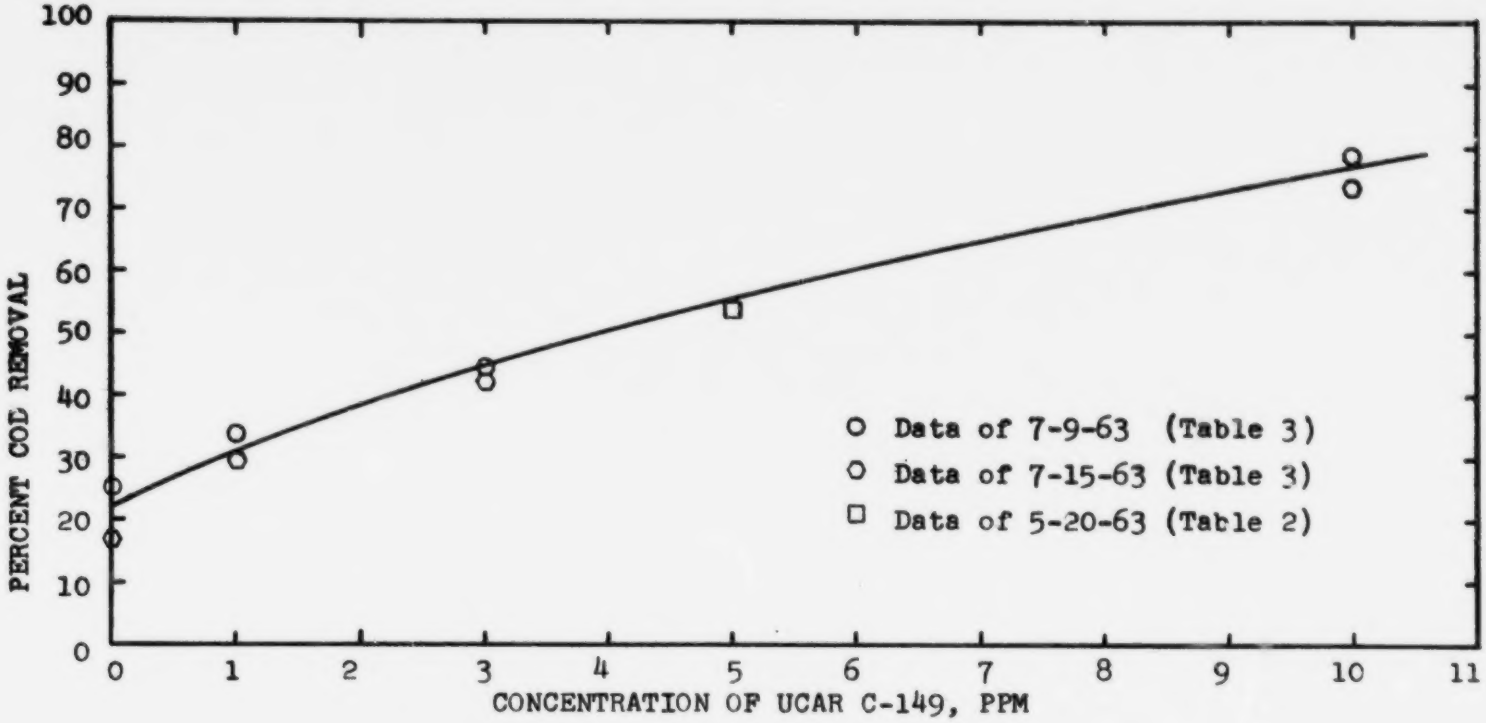
b
Heavy flocculation observed, solids accumulated on internal glass surfaces.

c
Good foaming, some deposition of coagulated solids on inner glass surfaces.

d
Poor foaming, unstable foam.

e
Samples mishandled, analyses discarded.

Figure 1. Effect of UCAR C-149 Concentration on COD Removal



effect of higher concentrations with 3 coagulants which did not perform very well in the screening studies at 5 ppm. The results indicate that although somewhat better performance is realized at 15 ppm, these materials still fall far short of the effectiveness of UCAR C-149 and Primafloc C-7 used at 10 ppm.

Another concentration effect which may be significant in the use of these cationic polyelectrolyte coagulants is the concentration of the coagulant solution added to the sewage effluent. This effect was touched on only briefly with a single set of 3 experiments on 10-17 (see Table 5 below). In these runs, the C-7 additive was used at the same overall concentration with respect to the effluent, but was diluted prior to use to 0.2 gm/liter compared with the concentration normally used (20 gm/liter). The data indicate poorer COD reductions with the more dilute additive solution.

Still another aspect of additive concentration was checked on 8-28 (Table 3). This set of runs was intended to show whether or not an additive could be made more effective at low concentrations by using it with an effluent which had already been subjected to foaming without the assistance of the additive. To the extent to which a single determination is meaningful, these runs indicate that a sequential 2-step foaming treatment using 5 ppm of UCAR C-149 in the second foaming is less effective in lowering both the COD and ABS than is the one-step operation even though the twice-foamed effluent was subjected to an overall G/F of 14 (7 for each operation) vs. only 7 for the once-foamed material.

4.1.2 Filtration vs. Foaming

Since the mechanism by which the cationic poly-

electrolytes improve COD and ABS reductions is coagulation, the question arises as to the best method for removing the coagulated solids. A brief series of experiments was conducted to examine the relative effectiveness of foaming and filtration as methods for removing the solids. Table 4 presents the data obtained from these runs.

In each case (for each sample of Bowery Bay primary effluent) two regular foaming runs were made, one without additive and one using 10 ppm additive. In addition, a third run was made in which the effluent was treated with 10 ppm of the additive and then filtered prior to foaming. Examination of the data reveals that in 2 of the 4 cases filtration of the coagulated solids produced a COD reduction equal to or greater than that obtained by foaming them out (sample F_3 vs. sample B_2). Thus it appears that, under the experimental conditions of this study, filtration was effective in removing the solids and that the COD improvement afforded by the additives is indeed largely due to the coagulation of the COD-contributing components. It is also to be noted that the ABS removals are effected primarily by foaming and not by filtration.

4.1.3 Coagulation Time

Since coagulating or flocculating operations are not instantaneous, it was of interest to determine the minimum time required for the cationic polyelectrolytes to be fully effective. All of the experiments reported above which used additives were performed by mixing a batch (several liters) of effluent with the proper amount of coagulant and agitating it for 1-1½ hours prior to feeding it (continuously) into the foaming apparatus. In order to determine the effect of coagulation time, it was necessary to feed the effluent and coagulant at appropriate rates

Table 4
Filtration vs. Foaming
(Flow rates were those listed in Table 3)

Date	Sample[a]	Additive Used: Name	Additive Used: Conc. ppm	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR dimensionless	Notes
8-16-63	F	-	-	1.7	400	582	1555	351	-	-
	B_1	None	-	0.7	361			235	d	-
	B_2	UCAR C-149	10	0.2	105			27	266	b
	F_3	UCAR C-149	10	1.6	200			40	-	c
	B_3	-	-	0.2	137			5	239	c
8-21-63	F	-	-	1.7	336	540	1326	267	-	-
	B_1	None	-	1.7	262			265	427	-
	B_2	UCAR C-149	10	0.2	206			60	128	-
	F_3	UCAR C-149	10	1.2	215			122	-	c
	B_3	-	-	0.2	202			59	185	c
8-26-63	F	-	-	1.0	332	1138	2211	291	-	-
	B_1	None	-	0.4	250			200	404	-
	B_2	Primafloc C-7	10	0.2	162			130	190	--
	F_3	Primafloc C-7	10	0.4	114			44	-	c
	B_3	-	-	0.2	116			94	171	c
9-12-63	F	-	-	2+	370	972	1846	182	-	-
	B_1	None	-	1.6	284			144	509	-
	B_2	Primafloc C-7	10	0.2	160			152	70	b
	F_3	Primafloc C-7	10	1.0	115	933	-	-	-	c
	B_3	-	-	0.2	124			56	248	c

[a] F = feed, effluent used.
B_1 = composite bottoms sample taken after 6 and 8 residence times during first run with the particular feed effluent.
B_2, B_3, etc. = same as B_1 except for second, third, etc., runs with the same feed
F_3 = feed for third run.

[b] Heavy flocculation observed, solids accumulated on internal glass surfaces.

[c] Effluent filtered after addition of coagulant, prior to foaming.

[d] Very high VR, very little foamate.

Table 5

Additional Experimental Data on Contaminant Removal from Sewage Plant Effluents
Effect of: Various Effluents, E
Air Rates, G
Feed Rates, F
Coagulation Time
Continuous Feeding of Coagulant
Use of Diluted Coagulant

Date	E	Additive Name[a]	Additive Conc. ppm	Sample	G ml/min.	F ml/min.	G/F	t_r min.	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR	Notes
9-18-63	BBS	-	-	F	390	56	7.0	8.3	1.9	91	972	2188	-	-	-
		None	-	B_1					0.8	27			-	86	-
		U	10	B_2					0.4	nil			-	73	b
		C-7	10	B_3					0.2	nil			-	68	b
9-20-63	BBS	-	-	F	390	56	7.0	8.3	2+	160	984	2225	e	-	-
		None	-	B_1					0.6	116			e	115	-
		U	10	B_2					0.4	46			e	234	b
		C-7	10	B_3					0.4	54			e	129	b
9-27-63	26S	-	-	F	390	56	7.0	8.3	1.9	205	850	4142	e	-	-
		None	-	B_1					0.4	233			e	143	-
		C-7	10	B_2					0.2	223			e	g	-
		U	10	B_3					0.2	195			e	92	-
10-3-63	26P	-	-	F	390	56	7.0	8.3	1.0	188	-	-	189	-	-
		None	-	B_1					0.4	116	-	-	167	218	-
		C-7	10	B_2					0.4	94	-	-	57	91	b
		U	10	B_3					0.2	113	-	-	63	403	b

continued

Table 5 (Continued)

Date	E	Additive Name[a]	Additive Conc. ppm	Sample[h]	G ml/min.	F ml/min.	G/F	t_r min.	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR	Notes
10-8-63	BBP	-	-	F	-	56	-	8.3	1.8	534	-	2954	366	-	-
		C-7	10	B_1	224		4.0		0.2	51			36	495	b
		C-7	10	B_2	390		7.0		0.2	41			nil	218	b
		C-7	10	B_3	355		9.9		0.2	79			nil	79	b
10-10-63	BBS	-	-	F	-	56	-	8.3	1.7	193	-	1583	342	-	-
		C-7	10	B_1	224		4.0		0.2	45			127[i]	459	b
		C-7	10	B_2	390		7.0		0.2	42			51[i]	141	b
		C-7	10	B_3	555		9.9		0.2	32			70[i]	77	b
10-14-63	BBP	-	-	F	-	56	-	8.3	2+	376	-	3192	-	-	-
		C-7	10	B_1	224		4.0		0.2	150				479	b,j
		C-7	10	B_2	390		7.0		0.2	136				122	b,j
		C-7	10	B_3	555		9.9		0.2	129				172	b,j
10-17-63	BBP	-	-	F	-	56	-	8.3	2+	345	-	-	-	-	j,k
		C-7	10[k]	B_1	224		4.0		1.2	211				400	b
		C-7	10[k]	B_2	390		7.0		0.8	190				111	b
		C-7	10[k]	B_3	555		9.9		0.4	171				195	b
10-21-63	BBS	-	-	F	-	56	-	8.3	2+	156	-	-	-	-	-
		C-7	10	B_1	224		4.0		1.8	-				406	b
		C-7	10	B_2	112		2.0		0.8	88				235	b
		C-7	10	B_3	168		3.0		0.4	80				163	b
10-23-63	BBS	-	-	F	-	56	-	8.3	2+	150	-	-	-	-	-
		C-7	10	B_1	224		4.0		1.0	122				264	-
		C-7	10	B_2	112		2.0		0.8	99				380	-
		C-7	10	B_3	168		3.0		0.4	49				380	-

continued

Table 5 (Continued)

Date	E	Additive Name[a]	Additive Conc. ppm	Sample	G ml/min.	F ml/min.	G/F	t_r min.	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR	Notes
10-25-63	BBP	-	-	F	-	56	-	8.3	2+	272	-	-	-	-	
		C-7	10	B_1	224		4.0		0.4	92				400	
		C-7	10	B_2	112		2.0		0.4	82				289	
		C-7	10	B_3	168		3.0		0.2	47				369	
10-31-63	BBP	-	-	F	390	56	7.0	8.3	2+	466	-	-	-	-	
		None	-	B_1					1.8	460				457	
		C-7	10	B_2					0.4	267				569	
		CF	10	B_3					0.8	112				338	
10-30-63	BBS	-	-	F	-	-	-		2+	240	-	-	-	-	
		C-7	10	B_1	224	56	4.0	8.3	0.8	330?				135	
		C-7	10	B_2	336	84	4.0	5.5	0.6	122				64	
		C-7	10	B_3	460	115	4.0	4.0	0.6	106				9.6	
11-4-63	BBP	-	-	F	-	-	-	-	2+	328	-	-	-	-	
		C-7	10	B_1	168	56	3.0	8.3	0.6	150				329	
		C-7	10	B_2	168	84	2.0	5.5	0.4	87				580	
		C-7	10	B_3	168	115	1.46	4.0	0.2	87				785	
11-6-63	BBS	-	-	F	-	-	-	-	2+	206[1]	-	-	-	-	
		C-7	10	B_1	168	56	3.0	8.3	0.6	118				256	
		C-7	10	B_2	168	84	2.0	5.5	0.4	145[1]				828	
		C-7	10	B_3	168	115	1.46	4.0	0.6	106				527	
11-11-63	BBP	-	-	F	-	-	-	-	2+	227	-	-	-	-	
		None	-	B_1	390	56	7.0	8.3	1.4	210				342	
		C-7	10	B_2	390	56	7.0	8.3	0.2	202				11	1) t_c=10 min
		C-7	10	B_3	390	84	4.6	5.5	0.2	197				11	1)

continued

Table 5 (Continued)

Date	E	Additive Name[a]	Additive Conc. ppm	Sample	G ml/min.	F ml/min.	G/F	t_r min.	ABS ppm	COD ppm	Cl^- ppm	TS ppm	SS ppm	VR	Notes
11-13-63	BBP	-	-	F	-	-	-	-	2+	378	-	-	-	-	
		None	-	B_1	390	56	7.0	8.3	2.0	367				20	
		C-7	10	B_2^2	390	56	7.0	8.3	0.4	175				33	1
		C-7	10	B_3	390	56	7.0	8.3	0.2	85				152	1,f } t_c=20 min
11-15-63	BBS	-	-	F	-	-	-	-	2+	114	-	-	-	-	
		None	-	B	390	56	7.0	7.3	0.8	62				294	
		C-7	10	B_1	390	56	7.0	7.3	0.2	59				21	1
		U	10	B_3^2	390	56	7.0	7.3	0.2	53				g	1 } t_c=20 min
11-20-63	BBP	-	-	F	-	-	-	-	2.0	464	-	2138	-	-	
		None	-	B_1	168	115	1.46	4.0	1.5	389	-	2086	-	g	
		U	10	B_2	168	115	1.46	4.0	0.6	107	-	1943	-	g	1, t_c=20 min

For Notes to Table 5, please refer to following page.

NOTES TO TABLE 5

a
Additives (coagulants):

U = UCAR C-149
S = SAC-154 (Union Carbide)
C-5 = Primafloc C-5
C-6 = Primafloc C-6 (Rohm & Haas)
C-7 = Primafloc C-7
F = Flocculant 614 (Dow Chemical Co.)
N = Nalcolyte 605 (Nalco Chemical Co.)

b
Heavy flocculation observed, solids accumulated on internal glass surfaces.

c
Good foaming, some deposition of coagulated solids on inner glass surfaces.

d
Poor foaming, unstable foam.

e
Samples mishandled, analyses discarded.

f
Effluent filtered after addition of coagulant, prior to foaming.

g
Very high VR, very little foamate.

h
F = feed, effluent used
B_1 = composite bottoms sample taken after 6 and 8 residence times during first run with the particular feed effluent
B_2, B_3, etc. = same as B_1 except for second, third, etc., runs with the same feed

i
Duplicate analyses differed widely.

j
Air bubbled into feed flasks to prevent settling of coagulated solids - in all runs after 10-14-63.

k
C-7 coagulant was diluted 100 times to 0.2 mg/ml vs. 20 mg/ml used in all other runs.

l
Coagulant and effluent fed separately and continuously into a mixing-coagulating beaker, and then to the column, continuously.

into a coagulation tank (beaker), to maintain a constant liquid hold-up in this tank so as to establish an average coagulation time, and to feed continuously from this tank into the foaming apparatus. This procedure was followed for the experiments performed on 11-11, 11-13, 11-15, and 11-20, the data from which runs are given in Table 5.

It is immediately apparent that 10 minutes is not long enough as an average coagulation time, since the additive runs using this t_c were not appreciably better than the straight foaming run. It is equally apparent that 20 minutes liquid hold-up time in the coagulation tank produces COD reductions equal to those achieved with batch coagulation times of 1-1½ hours.

Unfortunately, the time interval between 10 and 20 minutes was not studied in more detail, but a further optimization of the coagulation time required is more properly left for pilot plant studies.

4.1.4 Effectiveness of Additives with Secondary Effluents

Following the additive screening and concentration studies discussed above, it was considered desirable to check the effectiveness of UCAR C-149 and Primafloc C-7 when used with secondary effluents and with primary effluents from plants other than Bowery Bay. The runs of 9-18 and 9-20 listed in Table 5 show that these additives appear to be as helpful in reducing COD and ABS concentrations in Bowery Bay secondary effluents as in the primary effluents from this plant.

The experiments of 9-27 and 10-3, on the other hand, indicate that these same additives are essentially ineffective in improving COD reductions in both primary and secondary effluents from the 26th Ward Plant.

4.1.5 Economic Aspect of Additives

Although it is certainly not a process variable, the cost of the additives under study must be an important consideration in projecting their use in a foaming process for sewage treatment. The cationic polyelectrolytes, in a price range of $1.00 per pound, would represent an operating cost of about 8¢ per 1000 gallons if used at a concentration of 10 ppm. This cost must be compared with current secondary treatment (activated sludge) costs in the range of 6¢ to 8¢/1000 gallons.

4.2 Effect of Air and Effluent Flow Rates

Aside from the addition of coagulating agents discussed above (Section 4.1), the major controllable process variables in the foaming of sewage plant effluents are the flow rates of the two streams involved: air and effluent. The effects of these two flow rates and their ratio (G/F) have been discussed in some detail in the previous reports[1,2] of this program, but those earlier discussions were necessarily based on data considerably more limited in scope than those now available for analysis. The flow rate effects are re-examined here-first for Bowery Bay effluents modified by cationic polyelectrolyte coagulants and then for the (unmodified) effluents of 5 other plants.

4.2.1 Effect of Flow Rates in Systems Using Additives

The runs of 10-8, 10-14, and 10-25 (Table 5) were performed to show the effects of flow rate on the removal of ABS and COD from Bowery Bay Plant primary effluent modified by the addition of 10 ppm C-7, and the runs of 10-10, 10-21, and 10-23 were designed to do the same with samples of Bowery Bay secondary effluent. The results of these experiments are shown in slightly different form in Table 6.

These data appear to show a strong effect of G/F on COD removal from secondary effluents and little or no effect on the COD removal from primary effluents. It must be recognized, however, that duplicate runs gave widely differing results for different samples of effluent (primary runs 10-8 and 10-14, and secondary runs 10-10 and 10-23 for G=224 ml/min.), and that these "average" COD removal figures are based only on a few runs at best, and some on only single runs.

Table 6

Effect of Flow Rates on the Reduction of COD in Modified Bowery Bay Sewage Plant Effluents
(Constant Effluent Feed Rate = 56 ml/min.)

G ml/min.	G/F	Av. % COD Removal	
		Primary	Secondary
112	2	70.0(1)*	38.8(2)
168	3	82.7(1)	58.0(2)
224	4	72.2(3)	47.6(2)
390	7	78.0(2)	78.2(1)
555	9.9	75.4(2)	83.4(1)

* No. of runs used for average is given in parentheses

The experiments of 10-30 (Table 5) were carried out at a constant G/F but with varying liquid and gas rates.

Discarding the anomalous COD analysis for the bottoms of the first run (the duplicate analyses were in close agreement), it appears that improved ABS and COD reductions are attained at the higher G and F rates. As expected, the volume reduction suffers markedly at the higher rates if no changes are made in equipment geometry or liquid level to minimize liquid carry-over.

The effect of varying liquid rates at constant and relatively low air rates was examined on 11-4 and 11-6. Within

this low range of G/F's studied, better ABS and COD reductions were attained for both primary and secondary effluents at the higher liquid rates. These results are particularly interesting when considered in terms of liquid residence time (best results at the lowest residence times) and when compared with the data in Table 6 which appears to present conflicting data, indicating better COD reductions at higher G/F's (for secondary effluents). Apparently, when low liquid rates are used, high air rates promote better separations since a greater bubble surface area is presented for adsorbing and removing the suspended (and dissolved surface active) solids. The validity of the contradictory data of runs 11-4 and 11-6 should be checked before drawing a conclusion.

4.2.2 Effect of Flow Rates in the Foaming of Unmodified Effluents

It was determined early in this study[1] that the removal of ABS from unmodified effluents by foaming could be described for a given effluent by a plot of the bottoms (or final) ABS concentration as a function of the amount of air supplied per unit mass of ABS in the feed $\left[G/F(x_F)_{ABS}\right]$. It was later revealed,[2] however, that this correlation does not apply even individually to every sewage treatment plant and that it cannot be used to correlate the data from a number of plants. Apparently, there are plant-to-plant and even day-to-day compositional variations which exert a strong influence on ABS removal and which are not included in this correlation.

Several attempts have also been made to develop correlations for the effect of flow rates on COD reductions realized in the foaming of effluents. The first of these was applied only to secondary effluents from the 26th Ward Plant, and

even then it did not correlate the data particularly well: fractional COD reduction vs. $[G(x_F)_{COD}/F(x_F)_{ABS}]$. The second was applied both to primary and secondary effluents from the 26th Ward and Bowery Bay Plants and appeared to treat the data fairly well: COD concentration in the bottoms vs. COD concentration in the feed. This correlation indicated a generally constant fractional COD reduction (26%) regardless of flow rates.

Since all of this earlier work was limited to the use of effluents from only two plants, it became necessary to determine the efficacy of the foaming process when applied to effluents of widely different general characteristics (e.g., inland vs. coastal and domestic vs. industrial areas). For this purpose, samples of effluents from five other sewage plants were obtained and subjected to identical experimentation.

The plants from which effluents were obtained for this study are the following:

Cleveland Easterly, Ohio

Cleveland Southerly, Ohio

Whittier Narrows, California

Pomona, California

Nassau County, Long Island, New York

Samples of both primary and secondary effluents from each plant were included, and each sample was subjected to the following continuous-feed foaming treatment:

Apparatus: (See Section 6.)

Experimental Conditions:

Run	Feed (F) ml/min.	Air (G) ml/min.	G/F	Additive
A	56	280	5	None
B	56	448	8	None
C	56	616	11	None
D	115	575	5	10 mg/l*

* UCAR C-149 cationic polyelectrolyte coagulant (Union Carbide) was used for most runs.

The feed rates used correspond to average liquid residence times in the foaming unit of 8.3 minutes for Runs A, B, and C, and 4.0 minutes for Run D. The few exceptions to the listed experimental conditions are noted in Table 7 along with the experimental data.

The ABS results of these experiments are repeated in Figure 2 in accordance with the correlation mentioned above. It is immediately evident that this correlation is not at all suitable for treating this particular collection of data. It was found, however, that none of the numerous attempts to correlate these data yielded a really satisfactory presentation. A typical result of these efforts is shown in Figures 3 and 4 (suggested by the Project Officer for this Contract) which try to give the effect of G/F on ABS removal from primary and secondary effluents on separate graphs. The data points thus drawn do not allow the construction of a curve or line with any significance, but rather bracket the broad ranges of ABS removal which one might expect to realize when operating within the indicated ranges of G/F.

The COD reduction data from Table 7 are plotted as $(x_B)_{COD}$ vs. $(x_F)_{COD}$ in Figure 5. Again, it is quite apparent that this treatment does almost nothing toward correlating the experimental results. Since all other attempts to correlate these data were not satisfactory, they have been grouped and averaged for the individual plants, separately for primary and secondary effluents, in Table 8. Again, it must be stressed that Table 8 is not deemed to be an adequate picture of COD reduction by foaming, but it does at least demonstrate the very wide ranges of reductions which may be realized for the process conditions used in this study.

Any consideration of the data in Table 7 should include those runs in which 10 ppm of cationic polyelectrolyte were added to the feed. These results further substantiate the conclusions presented in Section 4.1 above: essentially that marked improvement in COD reduction may be expected with the use of these additives.

4.2.3 BOD Reduction by Foaming

Although the biochemical oxygen demand (BOD) is one of the most important quantities to be minimized by sewage treatment, essentially all of the experiments in this program used COD analyses as an indication of what might be happening to the BOD. This was done because of the relative ease of performing the COD analyses.

Several BOD analyses were performed for each of two sets of runs in Table 7, those for runs B and D on 1-24-64 and 1-29-64. These results are given in Table 9.

Table 7

Effects of Foaming on the Sewage Plant Effluents from Five Plants

Date	Plant[9]	Effluent[10]	Sample	ABS ppm	COD ppm	TS ppm	VR	Coagulation Time, hours	Notes
11-21-63	CE	S	F	2+	126	426	-		
			B_a	0.8	122	375	509		
			B_b	0.6	108	389	181		
			B_c	0.6	114	386	63		
			B_d	0.6	114	398	25		1
			B_e	0.4	87	412	25	1/3	2
11-27-63	CE	P	F	2+	260	517	-		
			B_a	1.7	213	486	521		
			B_b	1.5	214	509	700		
			B_c	1.0	191	492	255		
			B_d	0.8	180	653	-	1/3	3
12-3-63	CE	S	F	5.1	111	391	-		
			B_a	1.2	86	394	1317		
			B_b	0.6	42	373	149		
			B_c	0.4	19	382	115		
			B_d	1.8	108	422	-		4
12-9-63	CE	P	F	2.4	111	502	-		
			B_a	0.8	48	461	723		
			B_b	0.6	58	470	145		
			B_c	0.6	64	478	112		
			B_d	0.4	nil	414	33		
			B_e	0.2	nil	407	-	3	5
12-12-63	CS	P	F	9.5	220	836	-		
			B_a	3.0	143	710	118		
			B_b	2.4	125	715	80		
			B_c	1.8	152	719	64		
			B_d	1.6	94	662	58	1	

continued

Table 7 (Continued

Date	Plant[9]	Effluent[10]	Sample	ABS ppm	COD ppm	TS ppm	VR	Coagulation Time, hours	Notes
12-17-63	CS	S	F	4.5	121	619	-		
			B_a	2.4	101	620	204		
			B_b	0.6	97	633	102		
			B_c	0.4	90	540	29		
			B_d	0.4	105	562	46	3	6
12-20-63	CS	P	F	10.0	408	680	-		
			B	4.2	305	641	187		
			B^a	3.6	288	627	112		
			B^b	3.0	312	627	72		
			B^c	1.8	125	545	25	2½	
			B_d						
12-27-63	N	P	F	4.5	216	518	-		
			B_a	2.4	247	519	4480		
			B_b	0.6	207	535	172		
			B	3.6	228	520	160		
			B^c	0.8	132	498	100	2	6
			B_d						
12-30-63	N	S	F	4.5	62	399	-		
			B_a	1.8	46	380	172		
			B^b	1.2	38	400	34		
			B^c	1.2	27	390	12		
			B_d	0.8	15	376	9	2	
1-3-64	N	P	F	4.5	259	573	-		
			B_a	1.8	180	540	448		
			B^a	1.8	147	530	172		
			B^b	1.8	67	545	149		
			B^c	0.6	4	476	84	1½	
			B_d						
1-9-64	WN	S	F	2.8	74	550	-		
			B_a	1.8	63	540	448		
			B_b	0.8	63	541	75		
			B^c	0.8	52	535	52		
			B_d	0.8	26	538	115	1½	

continued

Table 7 (Continued)

Date	Plant[9]	Effluent[10]	Sample	ABS ppm	COD ppm	TS ppm	VR	Coagulation Time, hours	Notes
1-10-64	WN	P	F	5.4	315	743	-		
			B_a	2.4	188	700	224		
			B_b	1.8	188	705	149		
			B_c	1.8	186	695	75		
			B_d	0.6	85	632	-		
1-13-64	P	S	F	3.6	48	537	-		7,8
			B_a	1.8	37	531	280		
			B_b	1.2	30	624?	45		
			B_c	1.2	37	548	19		
			B_d	1.2	4	525	15		
1-15-64	P	P	F	10.0	300	829	-		
			B_a	5.4	185	-	64		
			B_b	4.8	78	-	30		
			B_c	3.9	100	-	22		
			B_d	1.2	92	-	12		
1-24-64	WN	P	F	4.8	217	603	-		7
			B_a	1.8	196	-	448		
			B_b	1.5	60?	-	112		
			B_c	1.2	160	-	56		
			B_d	0.6	100	-	15	1-2/3	
1-27-64	WN	S	F	4.8	195	560	-		
			B_a	1.8	83	-	149		
			B_b	1.2	56	-	50		
			B_c	1.2	56	-	32		
			B_d	1.2	29	-	46	2	
1-27-64	P	S	F	3.6	48	529	-		8
			B_a	1.8	4	-	187		
			B_b	1.2	24	-	59		
			B_c	1.2	4	-	41		
			B_d	1.2	12	-	34	2	
1-29-64	BB	P	F	-	304	1627	-		
			B_a	-	276	-	320		
			B_b	-	315	-	224		
			B_c	-	280	-	224		
			B_d	-	142	-	-	1-3/4	

Notes to Table 7

1. G = 575 ml/min, F = 115 ml/min, no additive.
2. G = 168 ml/min, F = 115 ml/min, 10 mg/l UCAR C-149.
3. Additive = 10 mg/l Primafloc C-7 (Rohm and Haas) added continuously to a mixing beaker.
4. Not a foaming run. 10 mg/l "Cat-floc" coagulant added to effluent, agitated for 23 minutes, and filtered.
5. Bottoms solution from D run filtered and refoamed, no extra additive used.
6. UCAR-C-149 added directly to effluent in solid form.
7. All suspended solids analyses rejected for this run.
8. Both secondary effluent samples from Pomona had been chlorinated.
9. Sewage Treatment Plants:

   CE = Cleveland Easterly, Cleveland, Ohio

   CS = Cleveland Southerly, Cleveland, Ohio

   N = Nassau County, New York

   WN = Whittier Narrows, California

   P = Pomona, California
10. Effluent: P = primary, S = secondary.

Table 8

Plant Averages of COD Reductions Achieved by Foaming
(in percent reduction)

Sewage Treatment Plant	Secondary Effluent		Primary Effluent	
	Range	Average	Range	Average
Cleveland Easterly	3.2-82.9	32.4	12.8-56.8	34.0
Cleveland Southerly	16.6-25.6	20.3	23.5-43.2	31.2
Nassau County	25.8-56.4	40.3	30.5-74.1	49.3
Whittier Narrows	14.8-71.3	43.2	9.7-41.0	31.5
Pomona	22.9-37.5	27.8	38.3-74.0	59.7

Table 9

BOD Reduction by Foaming

Date	BOD, mg/liter		
	Feed	B_b	B_d
1-24-64	115	75	42
1-29-64	172	131	48

These data demonstrate that foaming does lower the BOD, as well as the COD, of sewage plant effluents, that the BOD and COD reductions are very roughly similar, and that under the specific conditions checked the additive is quite effective in promoting BOD reduction, although not to a point comparable with standard secondary treatment (5-15 ppm).

Figure 2. Effect of Air Rate on Removal of ABS from Sewage Plant Effluents by Foaming

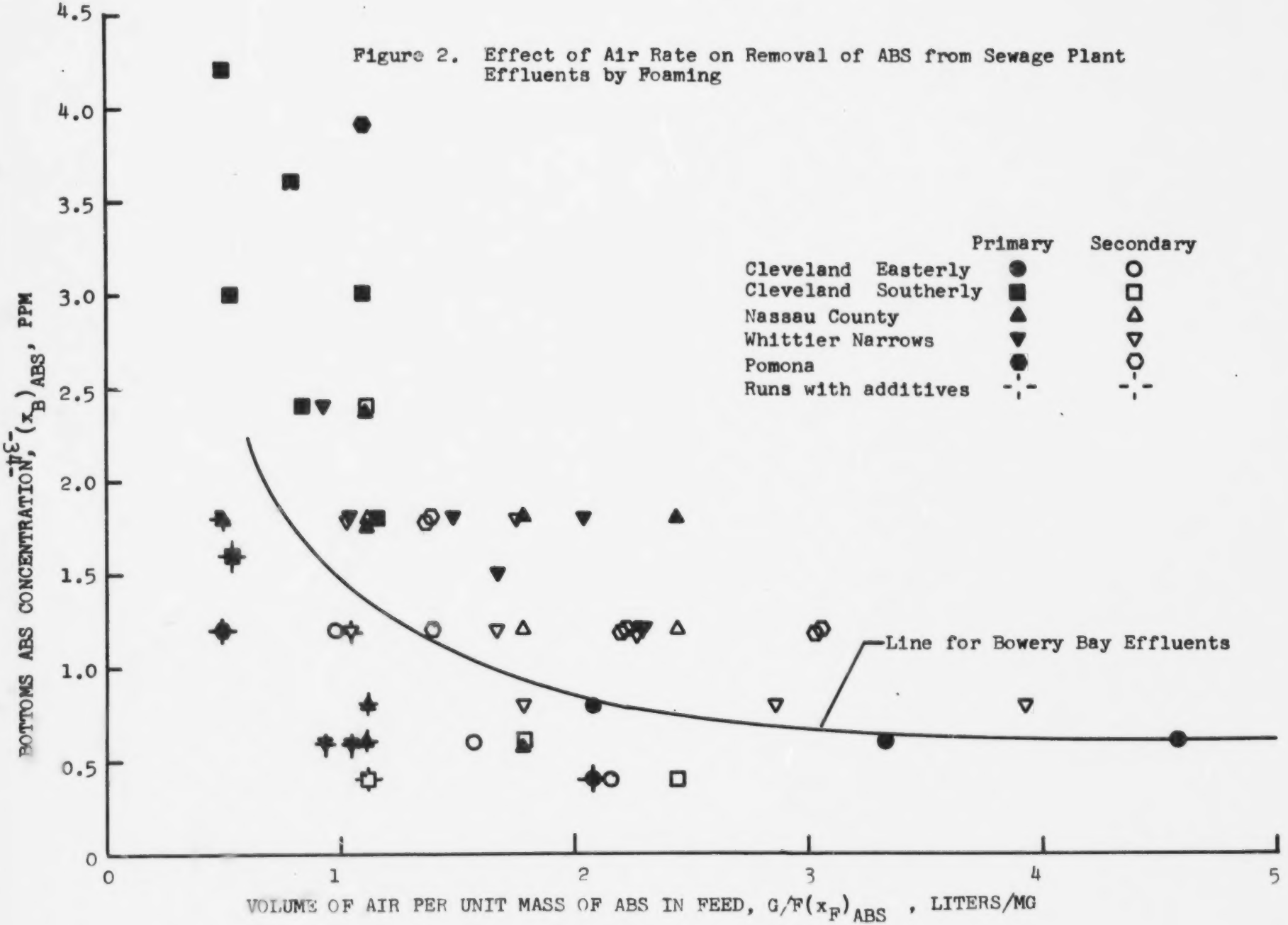


Figure 3. Effect of G/F on ABS Removal from Primary Effluents by Foaming

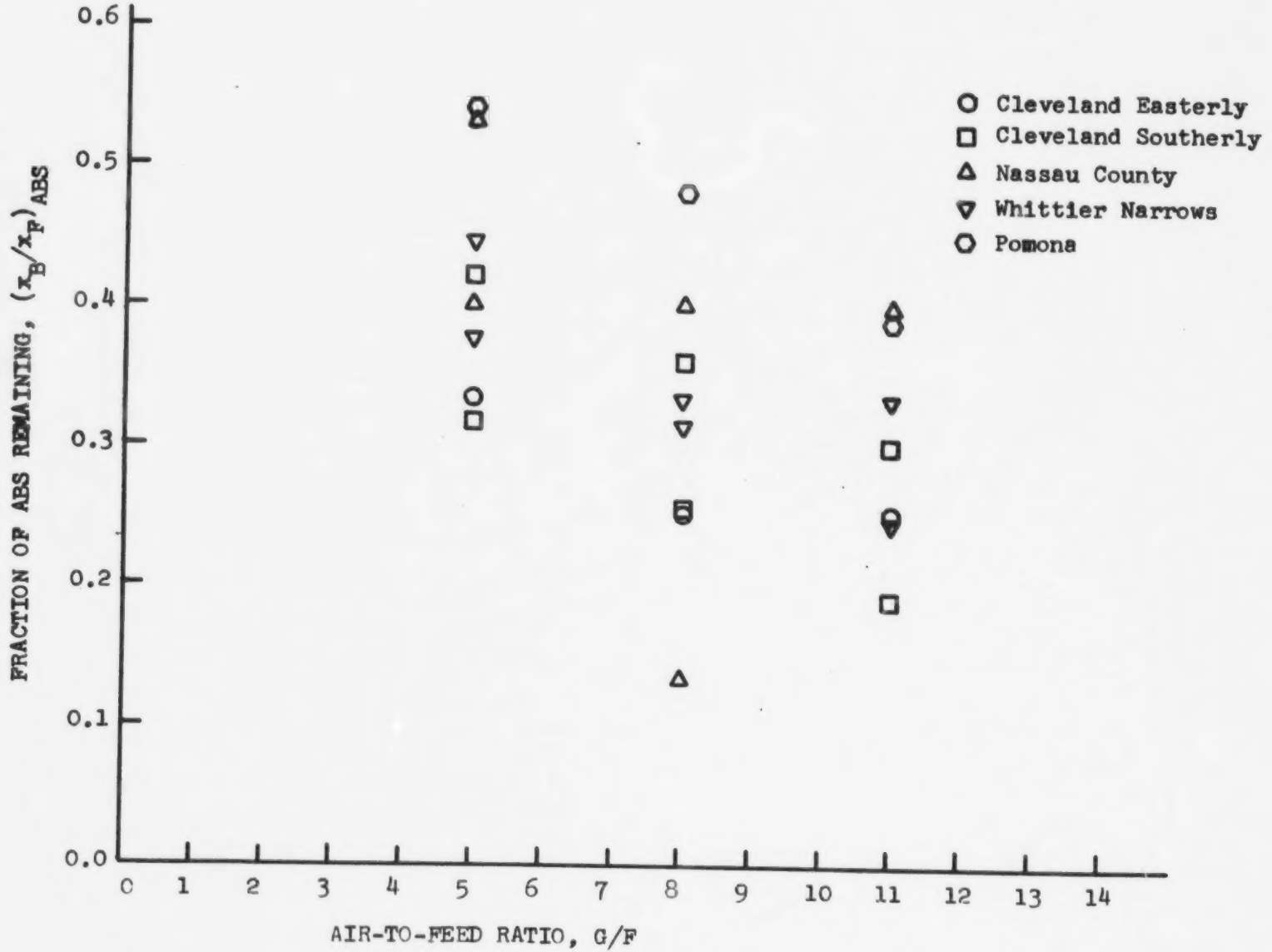


Figure 4. Effect of G/F on ABS Removal from Secondary Effluents by Foaming

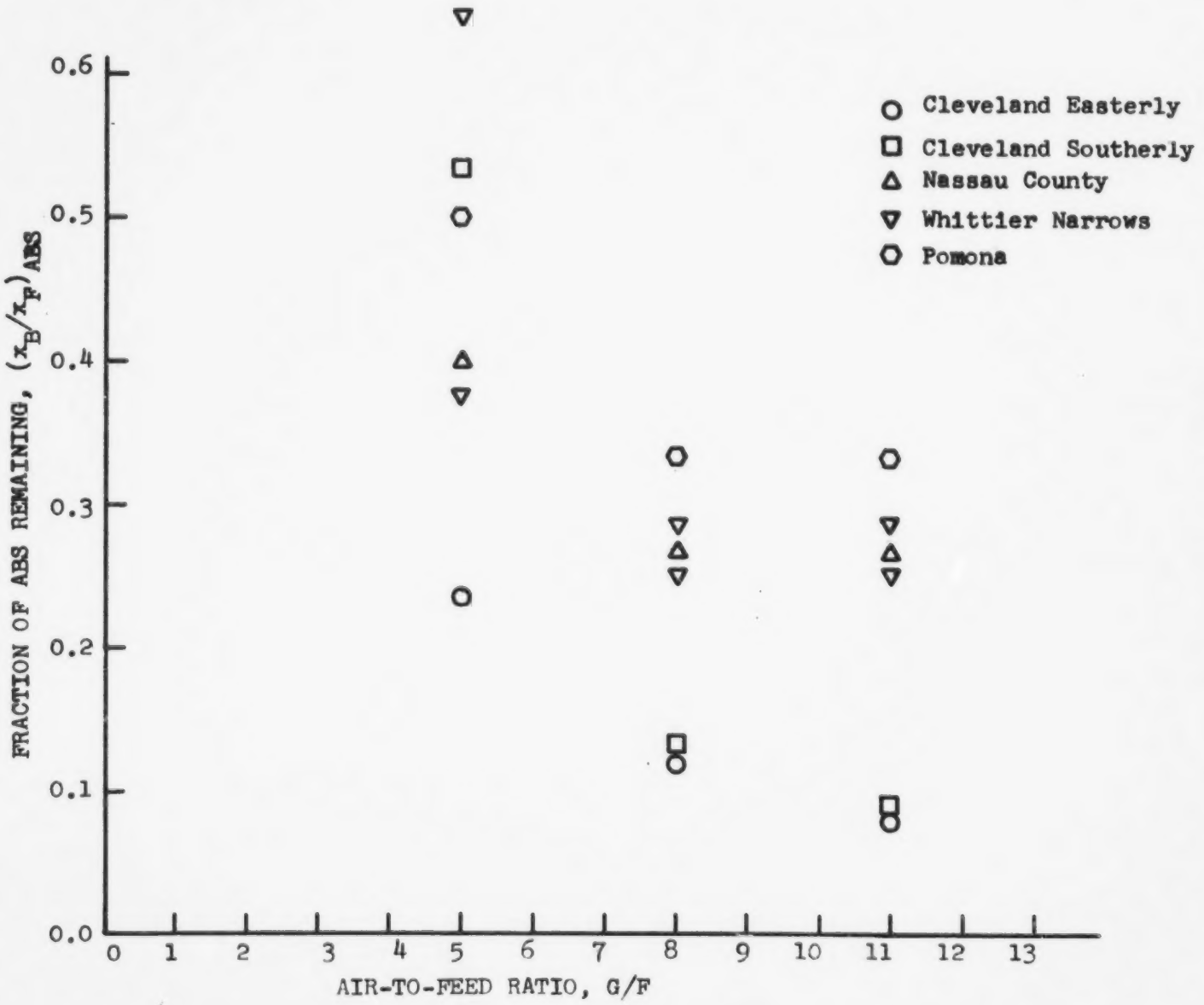
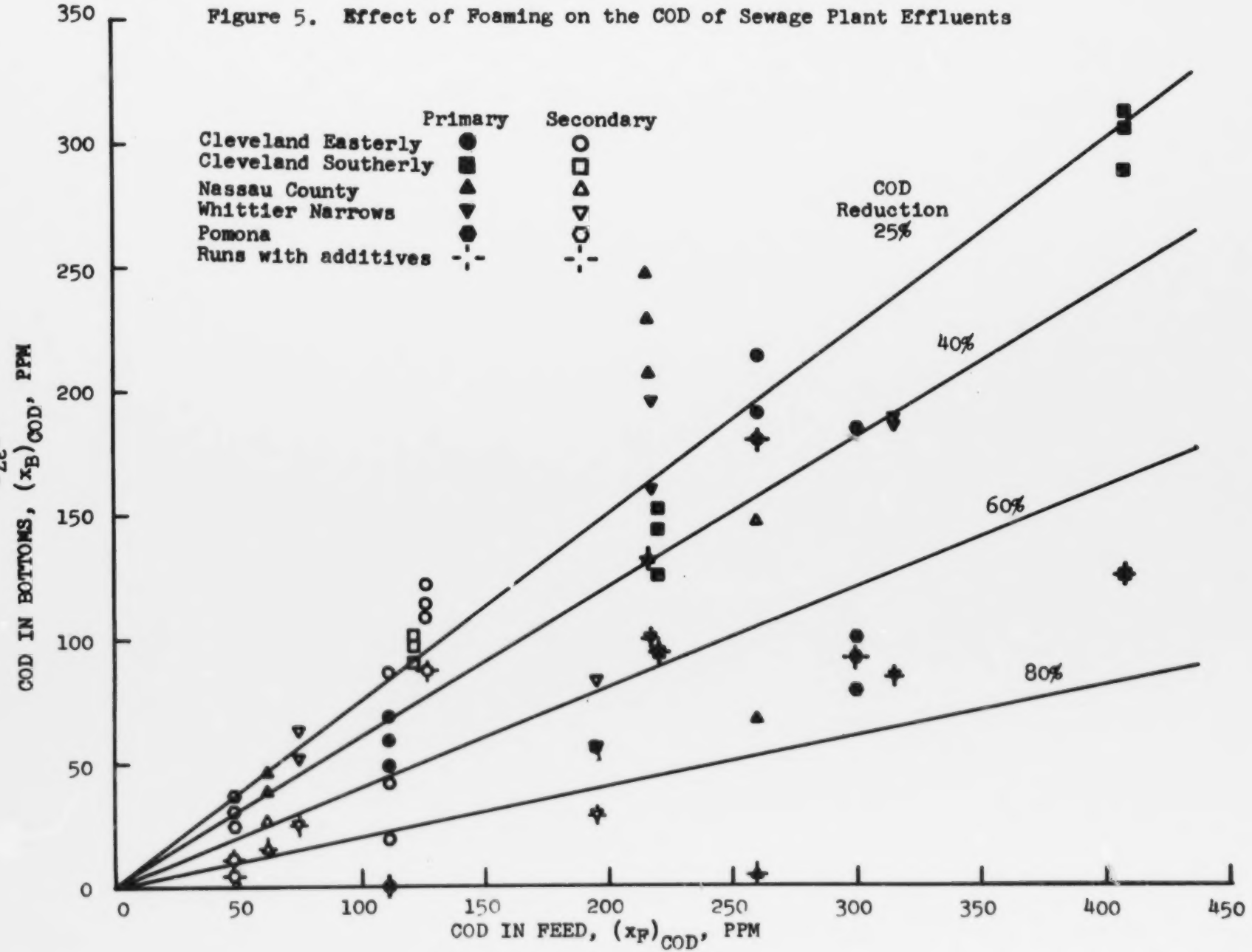


Figure 5. Effect of Foaming on the COD of Sewage Plant Effluents



5. FOAMING OF INDUSTRIAL WASTES

A brief final portion of this program was to have been devoted to the foaming of various industrial waste streams in order to develop a better understanding of the general types of specific plant wastes which might be "cleaned up" somewhat by a foaming treatment. In order to carry out this phase of the work, a considerable number of plants were contacted for the purpose of obtaining samples of their typical waste streams. Among them were breweries, dairies, refineries, and heavy chemical plants. In almost every single case, however, after an initial expression of interest and potential cooperation, we met with an amazing amount of resistance and hesitation with the result that no samples were obtained from these plants.

The only industry which was extremely cooperative was the pulp and paper industry through its National Council for Stream Improvement. From them we obtained two samples (we could have received others, but we were expecting samples from other industries at the time). The samples tested were Black Liquor, an effluent from a Kraft Mill pulping process, and de-inking washer water. The experimental apparatus was the same used for the sewage plant effluents described in Section 6. The results of these experiments, given in Table 10, show that foaming of these particular wastes under the conditions used did not effect any significant reduction in COD. It is to be noted, however, that both of these materials produced excellent stable foams. Thus, it may be possible to find a proper combination of foaming conditions and coagulant flocculating additive which will be effective in lowering the COD of these wastes.

Table 10

Foaming of Industrial Wastes

Expt.	Material	Sample[a]	F ml/min.	G ml/min.	ABS	COD
40	Black Liquor[c]	F	-	-	0.6	234
		B_1	56	280	0.6	205
		B_2	56	448	0.4	205
		B_3	28	308	0.2	198
		B_4[d]	115	515	0.2	202
41	De-inking Washer Water	F	-	-	b	1888
		B_1	56	280	b	1916
		B_2	56	448	1.8	1837
		B_3	28	308	1.2	1888
		B_4[d]	115	515	-	1888

[a] F = feed, effluent used
B_1 = composite bottoms sample taken after 6 and 8 residence times during first run with the particular feed effluent
B_2, B_3, etc. = same as B_1 except for second, third, etc., runs with the same feed.

[b] ppt in sample interfered with ABS analysis.

[c] Kraft Mill pulping effluent.

[d] 10 mg/liter of UCAR C-149 added.

6. EXPERIMENTAL APPARATUS AND METHODS

6.1 Experimental Procedures

The experimental apparatus consisted of the pyrex foaming apparatus shown in Figure 6. Three to four experiments were conducted with the same day's effluent. The first experiment was conducted with unmodified sewage effluent followed by two or three experiments with additives under the same experimental conditions.

Unmodified feed samples and composite bottoms samples were taken for analysis. The composite sampling technique involved mixing equal-volume bottoms samples taken after 6 and 8 residence times.

6.2 Analytical Procedures

Alkylbenzene sulfonate (ABS)

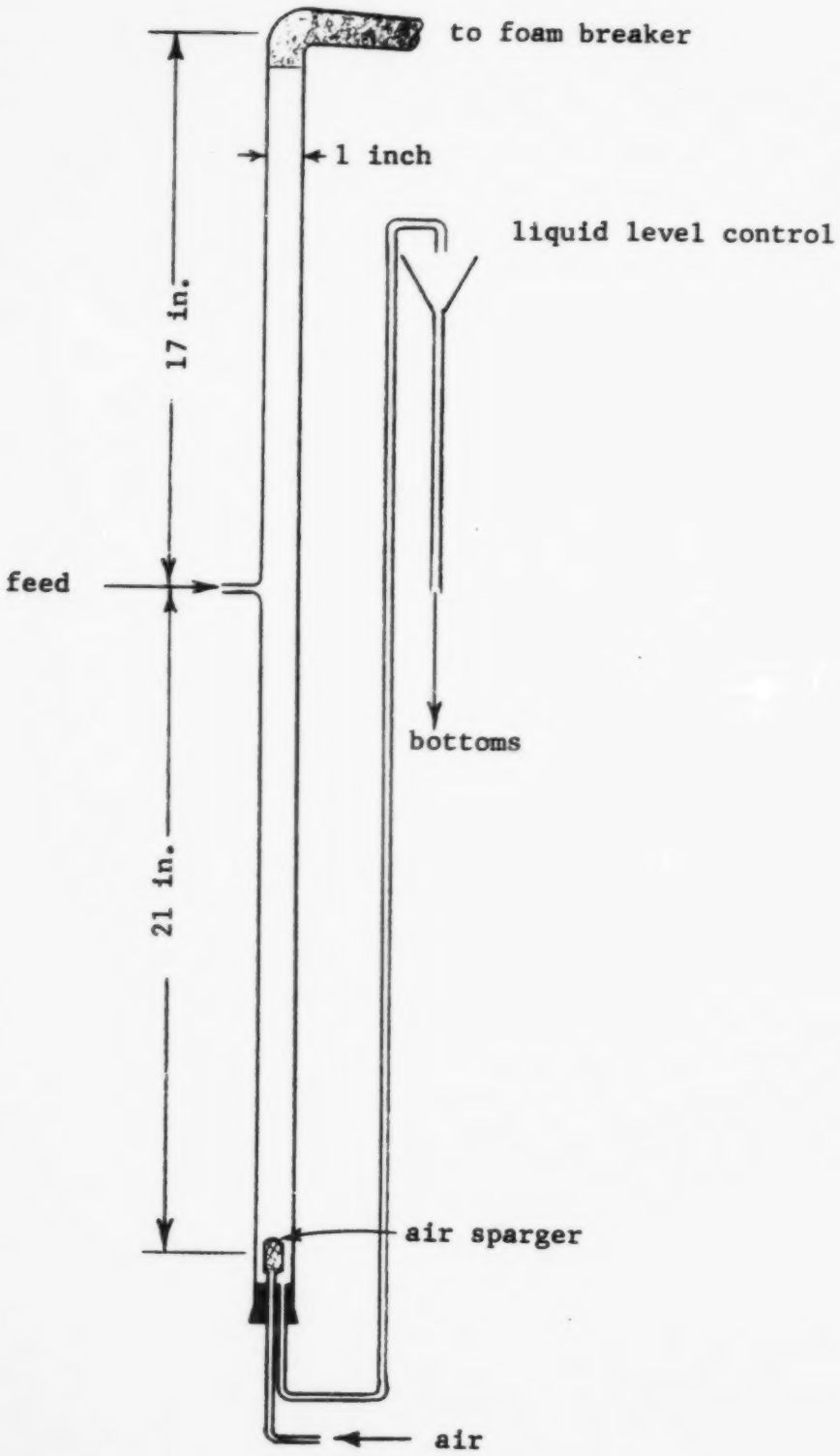
A simplified test procedure, using the Hellige Pocket Comparator (Hellige Inc., Garden City, N.Y.), was employed. The test is performed by measuring a sample into a simplified extraction bottle and adding measured amounts of methylene blue and chloroform. The mixture is shaken and the colored chloroform layer is poured into a tube. The color in the tube is compared with permanent glass color standards mounted in a color disc. The results are read directly in ppm.

The test procedure is less accurate than the standard methylene blue analysis. The reported ABS analytical data can be used, therefore, only as a general indication of experimental results.

Chemical Oxygen Demand (COD)

The modified COD test procedure, incorporating mercuric sulfate (no chloride correction) was used.

Figure 6. Diagram of Modified Laboratory Foaming Unit



Chloride (Cl^-)

The Volhard method was employed. Only unmodified feed was analyzed for chloride.

Total Solids (TS)

The procedure delineated in Standard Methods (pp. 326-7)[3] was followed. Only unmodified feed was analyzed for total solids.

Suspended Solids (SS)

The total suspended matter method delineated in Standard Methods (pp. 327-8) was followed.

Considerable inaccuracy in suspended solids determination was experienced when this analysis was introduced. The principal source of error was traced to insufficient accuracy in weighing. Starting June 11, 1963 all weighings for suspended solids determinations were carried out with an analytical balance accurate to 1/100 of a mg, with a resultant considerable improvement in accuracy.

7. REFERENCES

1. E. Rubin, R. Everett, Jr., J.J. Weinstock and H.M. Schoen, "Contaminant Removal from Sewage Plant Effluents by Foaming," Annual Report. Prepared for U.S. Public Health Service. Contract No. SAph 76555. October 15, 1962.

2. E. Rubin, R. Everett, Jr., and J.J. Weinstock, "Contaminant Removal from Sewage Plant Effluents by Foaming," Annual Report. Prepared for U.S. Public Health Service. Contract No. SAph 76555. August 1963.

3. Standard Methods for the Examination of Water and Waste Water, Eleventh Edition, American Public Health Association Inc., New York (1960).